



# Trimethyl borate and triphenyl borate as electrolyte additives for LiFePO<sub>4</sub> cathode with enhanced high temperature performance

Chia-Chin Chang<sup>a,\*</sup>, Kuan-Yi Lee<sup>b</sup>, Hsin-Ying Lee<sup>b</sup>, Yu-Hsiu Su<sup>b</sup>, Li-Jane Her<sup>c</sup>

<sup>a</sup> Department of Greenergy, National University of Tainan, Tainan 700, Taiwan

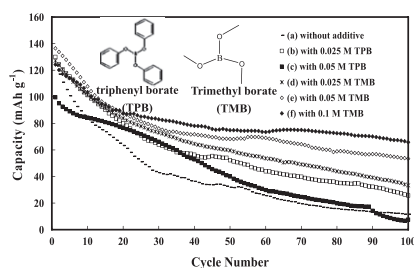
<sup>b</sup> Department of Material Science, National University of Tainan, Tainan 700, Taiwan

<sup>c</sup> Taiwan Hopax Chem. Mfg. Co., Innovation Development Center, No. 28, Hua Dong Road, Daliao, Kaohsiung 83162, Taiwan

## HIGHLIGHTS

- ▶ Trimethyl borate (TMB) has low participation in solid electrolyte interface (SEI).
- ▶ TMB is an effective electrolyte additive for the LiFePO<sub>4</sub> at 60 °C.
- ▶ Triphenyl borate (TPB) shows formation of a thick SEI which hampers Li<sup>+</sup> flow.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 October 2011

Received in revised form

1 May 2012

Accepted 28 May 2012

Available online 16 June 2012

### Keywords:

Lithium ion battery

Electrolyte additive

Triethylborane

Trimethyl borate

Lithium iron phosphate

## ABSTRACT

Alkyl- and phenyl-substituted borate anion receptors, triphenyl borate (TPB) and trimethyl borate (TMB), are investigated as electrolyte additives in lithium ion batteries (LiFePO<sub>4</sub> cathode, 1 M LiPF<sub>6</sub> EC-DMC 1:1 electrolyte) at 25 and 60 °C. TPB shows formation of a thick surface/electrolyte interface (SEI) which hampers ion flow and does not protect the electrode from degradation. Although useful at 25 °C, TPB at 60 °C results in only 7% capacity after 100 cycles, whereas 0.1 M TMB results in 53% capacity. TMB performance improves with increasing concentration. TMB also suppresses thermal decomposition of the electrolyte and formation of the SEI film.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

LiFePO<sub>4</sub> with an olivine structure has been studied extensively as a cathode material for lithium-ion batteries due to advantages such as low cost, good cycling performance at room temperature, high safety, non-toxicity and environmental friendliness. It is now popularly considered that LiFePO<sub>4</sub> has the most suitable cathode material characteristics for application in middle/large-size

electric vehicle (EV) and hybrid electric vehicle (HEV) batteries. But LiFePO<sub>4</sub> also exhibits capacity fading problems during cycling at elevated temperatures due to iron dissolution as well as the occurrence in the cell of impurities such as HF and H<sub>2</sub>O [1–5]. The presence of such impurities in LiPF<sub>6</sub> carbonate electrolytes with an LiFePO<sub>4</sub> cathode at elevated temperatures can promote iron dissolution of the LiFePO<sub>4</sub> surface and decompose the electrolyte, which then contributes to the formation of thick obstructive solid/electrolyte interphase (SEI) films [6,7]. Use of electrolyte additives is one of the most effective methods to protect against LiFePO<sub>4</sub> dissolution. Usually, no more than 5% by weight or by volume of a suitable additive is found to significantly improve cyclability of

\* Corresponding author. Tel.: +88662606123x7208; fax: +88662602205.  
E-mail address: [ccchang@mail.nutn.edu.tw](mailto:ccchang@mail.nutn.edu.tw) (C.-C. Chang).

Li-ion batteries [8]. Anion receptors have been proposed as electrolyte additives for lithium ion batteries for improved cycle life. Tris(pentafluorophenyl) borane (TPFPB) is an anion receptor which has been found to help in the dissociation of  $\text{LiPF}_6$  to  $\text{Li}^+$  and  $\text{PF}_6^-$  and found to mop up free  $\text{F}^-$  [9–12]. Further, addition of TPFPB results in decreased net formation of  $\text{LiF}$  in response to trace  $\text{H}_2\text{O}$  in the electrolyte, thus reducing corrosion of the electrode material by HF [9,10,13,14]. TPFPB achieves this by dissolving the normally insoluble  $\text{LiF}$ , which is an important factor because  $\text{LiF}$  decreases the conductivity of the SEI films [15,16]. TPFPB has been shown to reduce capacity fading and enhance cycling performance at 55 °C when used with commercial  $\text{LiPF}_6$  electrolyte in a  $\text{Li}/\text{LiMn}_2\text{O}_4$  cell [9,10,13,14]. Herstedt et al. reported that TPFPB additive can improve the thermal stability of a graphite anode [17]. Chang et al. reported that TPFPB can improve the cycling performance at elevated temperatures in  $\text{LiFePO}_4$  batteries with a  $\text{LiPF}_6$ -based electrolyte [6,7]. Other compounds based on alkyl borate compounds like tris(hexafluoroisopropyl) borate (THFPB) or tris(pentafluorophenyl) borate (TFPBO) have been investigated by McBreen et al. [12,18–21]. Recently, Chen and Amine reported on 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole as a bifunctional electrolyte additive for lithium ion batteries, with the additive acting both as a redox shuttle and an anion receptor [22]. The results from their report showed high cycling efficiency and cyclability with either  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  cathodes.

The anion-binding sites of additives based on borane or borate anion receptor compounds contain an electron-deficient B atom coordinated with electron-withdrawing groups. Such compounds have produced dramatic conductivity enhancement for a variety of lithium salts in low-dielectric constant, carbonate-based solvents systems such as are commonly used in rechargeable lithium batteries. Our research previously showed that a TPFPB electrolyte additive showed obvious improvement of high temperature cycle performance for  $\text{LiFePO}_4$  cathode material, an improvement attributed to decreased  $\text{LiF}$  content in the SEI film [6,7]. This study presents an investigation of the recent commercial alkyl-substituted borate anion receptors as additives for lithium battery electrolytes. The effects of alkyl- and phenyl-substituted borate anion receptors, namely triphenyl borate (TPB) and trimethyl borate (TMB), on anion coordination are compared. The electrochemical stabilities of these alkyl- and phenyl-substituted borate compounds are also evaluated. The effects of these compounds in an electrolyte in a (1:1 by weight) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) are characterized with regard to electrochemical performance and cycling stability of a  $\text{LiFePO}_4$  cathode at high temperature (60 °C). Finally, the electrolyte decomposition products on a  $\text{LiFePO}_4$  surface are characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

$\text{LiFePO}_4$  cathode material with carbon treatment was purchased (grade NO.1005, Changs Ascending Ent., Taiwan). Cathode electrodes were prepared by slurring the  $\text{LiFePO}_4$  material powder (91%) with 6% polyvinylidene fluoride (PVDF, Solef 6020, Solvay) and 3% Super P (MMM Carbon, Belgium) in an *N*-methylpyrrolidone (NMP, ISP) solvent. The mixed slurry was coated onto aluminum foil (20  $\mu\text{m}$ , Nippon Foil Co., Japan) and dried at 90 °C. The dried electrode was compressed by a roller at room temperature to make a smooth and compact film structure. Each preliminary electrode was punched to produce a candidate circular electrode disk of 1.368  $\text{cm}^2$  area. The resulting candidate disks were then weighed and measured for thickness. The loading of the cathode was

9.62  $\text{mg cm}^{-2}$  and the thickness was 60  $\mu\text{m}$ . Disks of similar weight and thickness were selected for further testing. These electrodes were placed under vacuum drying at 80 °C for 12 h. Finally, the prepared electrodes were stored in a glove box with oxygen and humidity content maintained below 5 ppm for more than 24 h before electrochemical characterization. The cathode electrodes were incorporated into coin type cells with a Li foil (FMC) anode electrode and Celgard separator (Celgard 2320). The reference electrolyte was a commercially available 1 M  $\text{LiPF}_6$  in an EC/DMC solvent (1:1 by weight ratio Ferro Corp.). All electrolytes were prepared in an argon glove-box (<5 ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$ ). The triphenyl borate (TPB, Strem Chemical) or trimethyl borate (TMB, Strem Chemical) additives at different concentrations were added in a 1 M  $\text{LiPF}_6$ /EC/DMC electrolyte, with the additive proportions strictly controlled. The chemical structures of TPB and TMB are shown in Fig. 1.

Cyclic voltammetry (CV) measurements were conducted with an Autolab electrochemical analyzer (Autolab PGSTAT30, Eco Chemie). The cells were assembled using a commercial three-electrode stainless steel test cell (HS test cell, Hohen Co.) with a 1  $\text{cm}^2$   $\text{LiFePO}_4$  cathode and lithium foil serving as both the counter and reference electrodes. The scan rate was 0.1  $\text{mV s}^{-1}$  at a voltage range between 2.5 and 4.2 V.

The electrode was disassembled inside a glove box from the coin cell and rinsed with DMC to remove the salts, then dried under vacuum at 25 °C for 24 h. Surface morphology of the  $\text{LiFePO}_4$  electrodes was evaluated by scanning electron microscopy (JEOL JSM35 operating at 20 kV) and the surface properties of the  $\text{LiFePO}_4$  electrodes were investigated by means of FTIR spectroscopy (Perkin–Elmer Spectrum 100 FTIR system inside a nitrogen-purged glove bag). The composition and structure of SEI formed on the  $\text{LiFePO}_4$  surface was determined by X-ray photoelectron spectroscopy (XPS, ESCA 210, V. G. Scientific Limited).

## 3. Results and discussion

To ascertain the effects of the various additive concentrations of TPB or TMB in the  $\text{LiPF}_6$ -based electrolyte (EC:DMC 1:1 by weight) on the electrochemical behavior, cyclic voltammograms of the  $\text{LiFePO}_4$  electrode in  $\text{LiPF}_6$ -based electrolyte without additive and with 0.05 M TPB or with 0.05 M TMB are shown in Fig. 2 curves (a), (b) and (c), respectively. The first cycle and second cycle are shown in Fig. 2(I) and (II), respectively. Fig. 2(I) curve (a) (without additive) shows that only one peak pair, consisting of one anodic peak ( $\text{Li}^+$  deintercalation) and one cathodic peak ( $\text{Li}^+$  intercalation), a behavior which corresponds to the two-phase charge/discharge reaction of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple [7,23]. For the electrolyte with either additive, the shift of the voltage peaks in the anodic direction shows that both additives appear to participate in passivation reactions of the  $\text{LiFePO}_4$  electrode and affect the lithium ion transfer rate. This result is related to TPB's and TMB's molecular

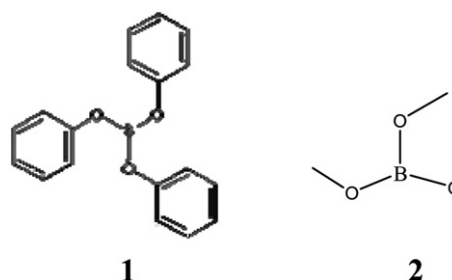


Fig. 1. Chemical structure of: (1) triphenyl borate (TPB); (2) trimethyl borate (TMB).

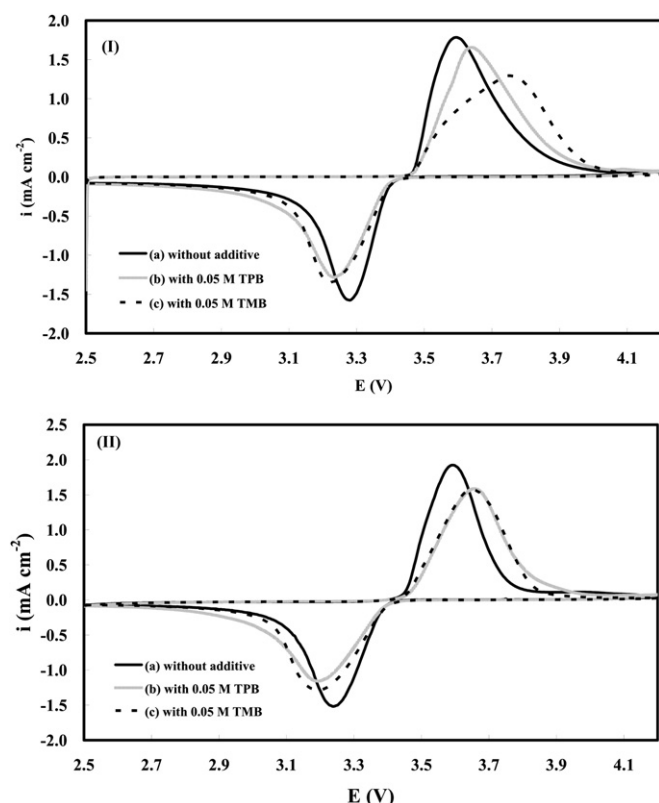


Fig. 2. Cyclic voltammograms of LiFePO<sub>4</sub> electrodes at (I) 1st and (II) 2nd cycles in 1 M LiPF<sub>6</sub> EC-DMC (1:1) solution: (a) without additive; (b) with 0.05 M TPB; (c) with 0.05 M TMB. Scan rate: 0.1 mV s<sup>-1</sup>. Voltage range: 2.5–4.2 V.

structure, since both possess an electron-deficient B atom coordinated with electron-withdrawing groups. The electron-deficient B atom will coordinate with PF<sub>6</sub><sup>-</sup>. The triphenyl or trimethyl groups influence the behavior of the electron-deficient of B atom. The trimethyl borate (TMB, curve (c)) in Fig. 2(I) shows a broad peak at approximately 3.73 V. The TPB peak (curve b) in Fig. 2(I) is similar to the behavior of the electrolyte without additive, but the TPB peak shows a small shift in the direction of higher voltage. The charge of the oxidation and reduction peaks is calculated for each scan. The charge of the oxidation peak represents lithium deintercalation from LiFePO<sub>4</sub> and the reaction between the electrolyte and electrode surface. The charge of the reduction peak represents intercalation of lithium into LiFePO<sub>4</sub>. The values are normalized as percentages and shown in Table 1. The differences of the integrated areas of the oxidation and reduction (O–R) signals at scan 1 for the various additives decrease in the following order: without additive > TPB > TMB. For the differences of the integrated areas of the O–R signals at scan 2, the values of the electrolyte with additives are smaller than the without additive case. These results show

that TMB can reduce the reaction between the electrode surface and the electrolyte.

The first charge and discharge capacities of LiFePO<sub>4</sub> in the electrolyte without and with additive are shown in Table 2. The TPB additive can be prepared only to 0.05 M due to the solubility limit. The irreversible capacity ratio of LiFePO<sub>4</sub> in the electrolyte without additive reaches as high as 18.32%. For the electrolyte with TPB or TMB, the discharge capacities increase slightly and the irreversible capacity ratio is reduced with increasing concentration of additive. These results are attributed to the additives reducing or preventing reaction of impurities such as HF, H<sub>2</sub>O and R–OH with electrolyte components such as EC, DMC and PF<sub>6</sub><sup>-</sup>. Such reactions contribute to formation of a performance-degrading SEI on the LiFePO<sub>4</sub> surface, and also tend to dissolve Fe-ions into the electrolyte from the impurities containing iron atoms in the LiFePO<sub>4</sub> raw material [5,24]. The performance of TMB is seen to be better than TPB.

To further confirm the effects of the electrolyte additives with regard to improving the cycling performance of Li/LiFePO<sub>4</sub> cells, the discharge capacities vs. cycle number at 25 and 60 °C are shown in Figs. 3 and 4, respectively. It can be seen from Fig. 3 that when TPB or TMB are added, they enhance the discharge capacity as a result of enhanced reversible capacity. The capacity loss after 100 cycles at 25 °C is 37% for 0.05 M TPB, which is worse than for the TMB additive and without additive cases (Fig. 3(II)). Higher temperature enhances reaction between the electrolyte and the electrode surface. Fig. 4 shows that, without either additive in the electrolyte, the capacity fades quickly at 60 °C cycling. TPB is seen to provide some high temperature protection, but the protection provided by TPB also fades quickly. In contrast, the TMB additive significantly reduces the problem of high temperature cycle fading, with the protection remaining active for a long period of time. Moreover, the cycling performance of LiFePO<sub>4</sub> increases with increasing concentration of TMB in the electrolyte. The capacity loss with 0.1 M TMB after 100 cycles at 60 °C is 47%. The electrolyte with 0.05 M TPB, on the other hand, essentially fails to inhibit the reaction between the electrolyte and electrode surface, with the discharge capacity ratio after 100 cycles at 60 °C being only 7% of the first discharge capacity. It is thus seen that the LiFePO<sub>4</sub> electrode in the LiPF<sub>6</sub>-based electrolyte with the 0.1 M TMB additive maintains good high temperature cycling performance. It is assumed that trimethyl borate participates in formation of a modified SEI film which contains less LiF, thereby improving capacity retention. TPB, conversely, is not effective in removing LiF from the SEI film on the LiFePO<sub>4</sub> electrode surface at high temperature.

The impedance of the cathode electrode with the different electrolyte additives also can be observed by AC impedance spectroscopy. All cells are measured after constant-current (0.1 C) charging to 4.2 V. The results with the various additives after 100 cycles at 60 °C are shown in Fig. 5. Comparison shows that the interfacial impedance of the cells with the TPB additive after 100 cycles at 60 °C is much higher than that with the TMB additive and

Table 1  
Ratio of oxidation/reduction peak areas on cyclic voltammetry. The oxidation peak integral is from 3.3 to 4.2 V. The reduction peak integral is from 3.5 to 2.6 V.

Additive	Oxidation scan 1 (%)	Reduction scan 1 (%)	Oxidation <sup>a</sup> scan 2 (%)	Reduction <sup>b</sup> scan 2 (%)	O–R scan 1 (%)	O–R scan 2 (%)
LFP-blank	0.568	0.432	0.534	0.466	0.137	0.068
TPB	0.564	0.436	0.520	0.480	0.129	0.041
TMB	0.562	0.438	0.512	0.488	0.124	0.024

<sup>a</sup> Oxidation% = (Oxidation)/(Oxidation + Reduction) × 100%.

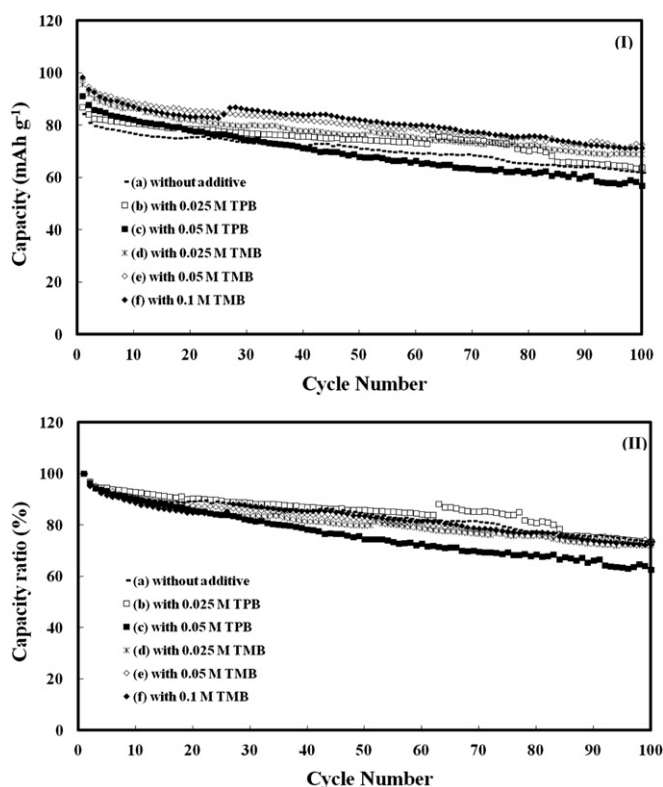
<sup>b</sup> Reduction% = (Reduction)/(Oxidation + Reduction) × 100%.

Table 2

First charge and discharge capacities of LiFePO<sub>4</sub> in 1 M LiPF<sub>6</sub> in EC/DMC (1:1) electrolyte without/with TPB, or TMB additives. The cells were cycled between 2.5 and 4.2 V at 0.1 C.

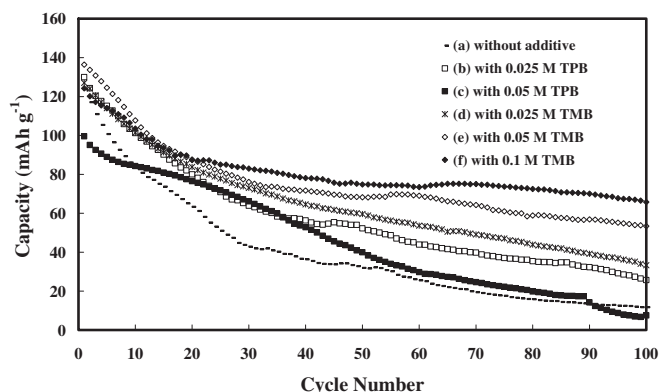
Additive	Concentration (M)	Charge (mAh g <sup>-1</sup> )	Discharge (mAh g <sup>-1</sup> )	Irr (%) <sup>a</sup>
LFP-blank	—	142.07	116.04	18.32
TPB	0.025	148.31	122.64	17.31
	0.05	149.51	129.33	13.50
TMB	0.025	153.47	123.35	19.63
	0.05	147.47	130.58	11.45
	0.1	140.61	125.14	11.0

<sup>a</sup> Irreversible capacity ratio = (charge capacity – discharge capacity)/(charge capacity) × 100%.

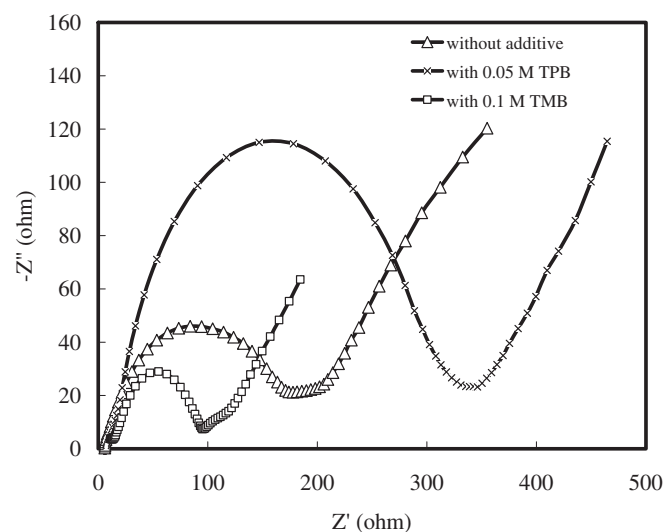


**Fig. 3.** Discharge capacity (I) and cycling efficiency (II) of LiFePO<sub>4</sub> electrodes at 25 °C in 1 M LiPF<sub>6</sub> EC-DMC (1:1): (a) without additive; (b) with 0.025 M TPB; (c) with 0.05 M TPB; (d) with 0.025 M TMB; (e) with 0.05 M TMB; (f) with 0.1 M TMB. Charge/discharge is at 1 C rate. Voltage range: 2.5–4.2 V. The cycling efficiency is calculated as the discharge capacity of the cycles divided by the discharge capacity of the first cycle.

without additive. The observed results are assumed to relate to formation of a modified SEI and the dissolution of LiF. LiF is almost insoluble in most organic solvents and is well known to be a nonconductor of both electrons and lithium ions [5,12,25]. However, it seems that TPB does not assist in dissolving LiF and also obstructs charge transfer. Addition of additional TPB produces poorer results. It is speculated that TPB or its reaction products are incorporated into the SEI film during the formation reaction, with this effect being amplified by higher temperature. These results show that TMB is a stronger anion complexing agent than TPB,



**Fig. 4.** Cycling performance of LiFePO<sub>4</sub> electrodes at 60 °C in 1 M LiPF<sub>6</sub> EC-DMC (1:1): (a) without additive; (b) with 0.025 M TPB; (c) with 0.05 M TPB; (d) with 0.025 M TMB; (e) with 0.05 M TMB; (f) with 0.1 M TMB. Charge/discharge at 1.0 C rate. Voltage range: 2.5–4.2 V.



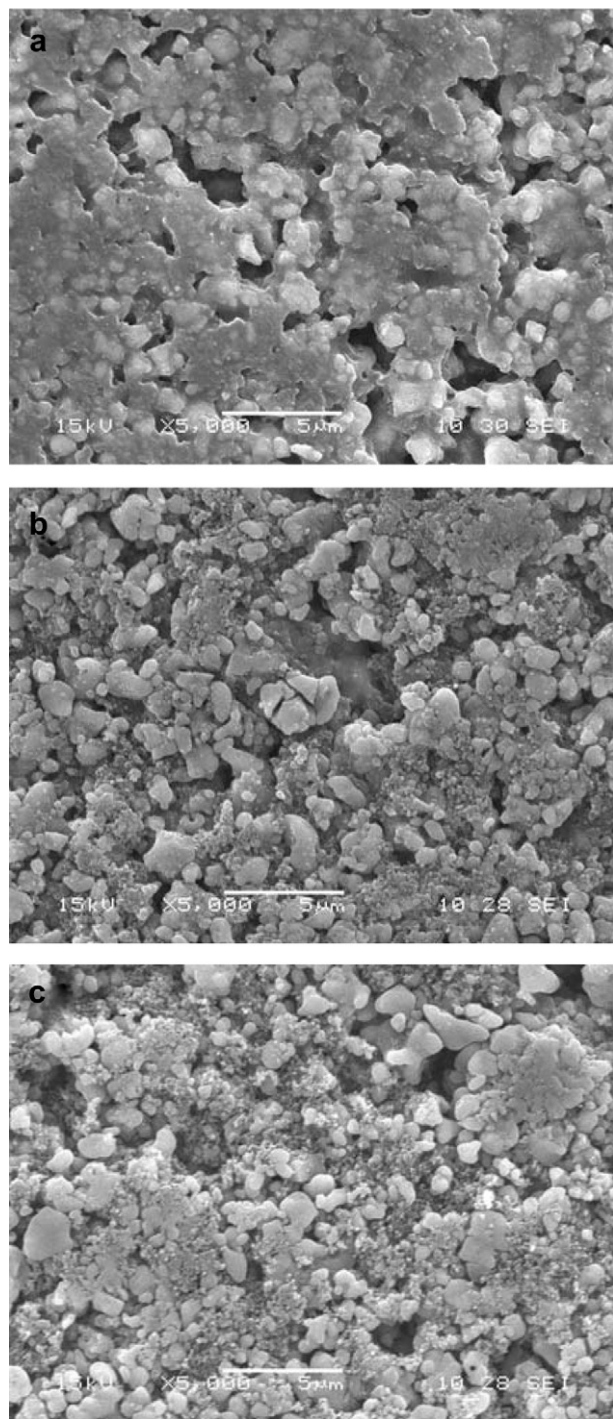
**Fig. 5.** Impedance spectra of fully delithiated LiFePO<sub>4</sub> electrodes in 1 M LiPF<sub>6</sub> EC-DMC (1:1) after 100 cycles at 0.1 C charge/discharge and 60 °C: (Δ) without additive; (×) with 0.05 M TPB; (□) with 0.1 M TMB. Frequency range: 0.01 Hz and 10<sup>6</sup> Hz.

inhibiting electrolyte decomposition and removing LiF from the SEI film on the LiFePO<sub>4</sub> surface.

To help clarify the surface morphology and behavior of the electrode, Fig. 6 shows  $\times 5000$  SEM micrographs of the LiFePO<sub>4</sub> electrodes: (a) with 0.05 M TPB additive after 100 cycles at 60 °C in 1 M LiPF<sub>6</sub> EC-DMC (1:1); (b) with 0.1 M TMB after 100 cycles at 60 °C in 1 M LiPF<sub>6</sub> EC-DMC (1:1); (c) a pristine electrode with no electrolyte and no cycling. Nano-size conductive carbon can be seen on the pristine electrode. Fig. 6(a) shows a distinct cohesive film on the LiFePO<sub>4</sub> electrode after 60 °C cycling with 0.05 M TPB additive. Adding more TPB results in worse performance, suggesting that TPB or its reaction products are anti-productive within the film. In contrast, the electrode cycled with 0.1 M TMB (Fig. 6(b)) shows large smooth LiFePO<sub>4</sub> particles with an overall appearance similar to the pristine electrode (Fig. 6(c)). This indicates that 0.1 M TMB additive assists in dissolution of LiF and helps in the dissociation of LiPF<sub>6</sub> to Li<sup>+</sup> and PF<sub>6</sub><sup>-</sup>. The above results show that TMB decreases the formation of surface films in response to nucleophilic surface oxygen anions attacking electrophilic RO(CO)OR in the electrolyte and H<sub>2</sub>O and HF trace impurities in the LiFePO<sub>4</sub> lithiated state, thus forming surface species such as ROCO<sub>2</sub>Li, ROLi, LiF, etc. [5,9–14,24]. During the cell charge–discharge cycle, TMB enhances the capacity utilization rate of the LiFePO<sub>4</sub> electrode and helps maintain cyclability at 60 °C.

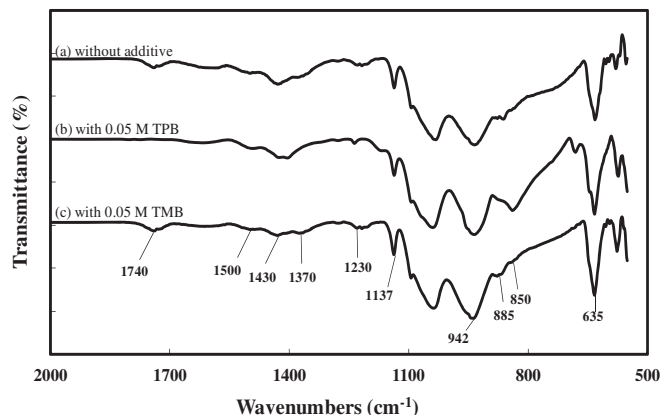
Use of diffuse FTIR reflectance mode spectroscopy allows further comparison of the electrode surfaces. Fig. 7 displays the FTIR patterns of a LiFePO<sub>4</sub> cathode with LiPF<sub>6</sub>-based EC/DMC electrolyte after 100 cycles at 60 °C under the following conditions: (a) without additive; (b) with 0.05 M TPB; (c) with 0.05 M TMB. The FTIR spectrum of olivine LiFePO<sub>4</sub> (Fig. 7(a)) demonstrates broad maximum peaks between 900 and 1200 cm<sup>-1</sup>, which can be assigned to P–O vibrations of the PO<sub>4</sub><sup>3-</sup> polyanion for FePO<sub>4</sub> while the absorption at 1137 cm<sup>-1</sup> originates from symmetric and anti-symmetric stretching vibrations of O–P–O [2,26,27]. The absorption around 942 and 635 cm<sup>-1</sup> originates from stretching P–O vibration [2]. The peaks around 1500–1420 cm<sup>-1</sup> are assigned to Li<sub>2</sub>CO<sub>3</sub> groups by Aurbach [28]. These materials on the electrode surface may be attributed to LiFePO<sub>4</sub> surface reaction with EC, DMC, LiPF<sub>6</sub>, etc., decomposing electrolyte components and the formation of polycarbonates (e.g. the  $\nu_{\text{CH}_2\text{CH}_3}$  peaks around 1450–1300 cm<sup>-1</sup>, the  $\nu_{\text{C=O}}$  peaks around 1800–1600 cm<sup>-1</sup>, the  $\nu_{\text{LiPF}_6}$  salt peaks at 848





**Fig. 6.** SEM micrographs ( $\times 5000$ ) of the  $\text{LiFePO}_4$  electrode: (a) with 0.05 M TPB after 100 cycles at 60 °C; (b) with 0.1 M TMB after 100 cycles at 60 °C; (c) a pristine electrode with no electrolyte and no cycling.

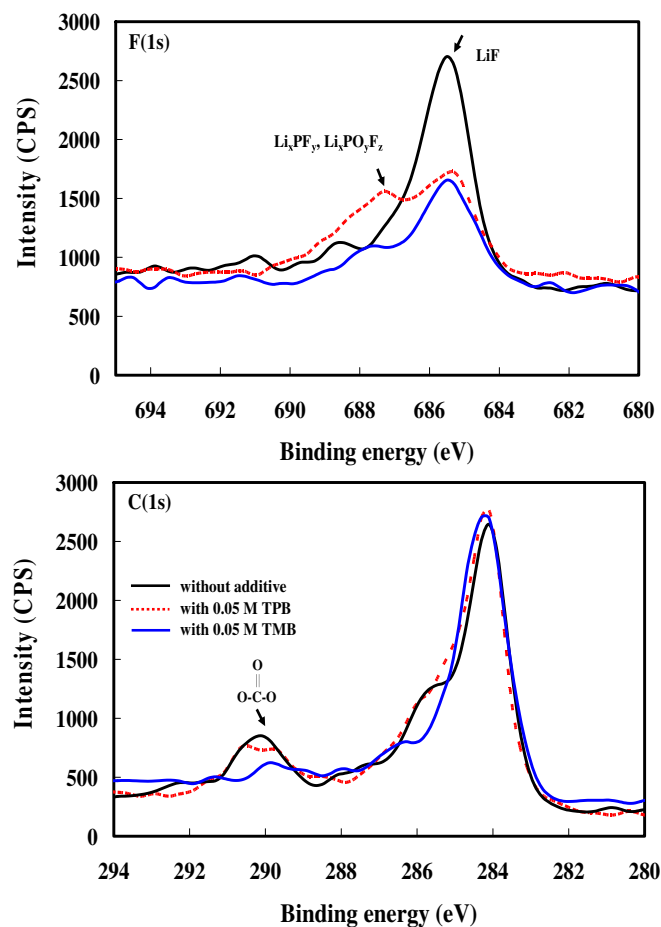
and  $559\text{ cm}^{-1}$ ) on the electrode surface [7]. The TMB curve has reduced SEI peak intensities, indicating that TMB reduces SEI formation on the  $\text{LiFePO}_4$  surface. TPB (Fig. 7(b)) does not protect the electrolyte components from decomposition. TPB also show a significant difference around  $885\text{--}850\text{ cm}^{-1}$ , which is assumed to indicate contributions by P–F bonds [29]. The peaks around  $1300\text{--}1100\text{ cm}^{-1}$  are attributed to species with a  $\text{Li}_x\text{PF}_y\text{O}_z$  bending mode and LiF. SEI film formation under the tested conditions is known to involve ethylene carbonate and diethyl carbonate



**Fig. 7.** FTIR spectra of  $\text{LiFePO}_4$  electrode in 1 M  $\text{LiPF}_6$  EC-DMC (1:1) after 100 cycles at 60 °C: (a) without additive; (b) with 0.05 M TPB; (c) with 0.05 M TMB.

participation, which decompose and produce a mixture of organic species that include polycarbonates,  $\text{LiF}$ ,  $\text{Li}_x\text{PF}_y$ -type and  $\text{Li}_x\text{PF}_y\text{O}_z$ -type compounds, and further may become  $\text{Li}_2\text{CO}_3$  and alkanes [30–32].

Complementary information was obtained from XPS measurements. Fig. 8 shows that the F 1s and C 1s spectra of a  $\text{LiFePO}_4$  cathode with  $\text{LiPF}_6$  based EC/DMC electrolyte after 100 cycles at



**Fig. 8.** XPS spectra of the F 1s and C 1s states of  $\text{LiFePO}_4$  electrode in 1 M  $\text{LiPF}_6$  EC-DMC (1:1) after 100 cycles at 60 °C: (a) without additive; (b) with 0.05 M TPB; (c) with 0.05 M TMB.

60 °C under the following conditions: (a) without additive; (b) with 0.05 M TPB; (c) with 0.05 M TMB. The F 1s spectra demonstrate the formation of surface LiF from the presence of the peak at 685–686 eV. The results show that the amount of LiF on the LiFePO<sub>4</sub> in the electrolyte without additive after 100 cycles at 60 °C is larger than that in the electrolyte with 0.05 M TMP or TPB additives. Other fluorine compounds with a higher oxidation state of the fluorine atoms at 689–687 eV, may reflect the formation of surface Li<sub>x</sub>PF<sub>y</sub> or Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> species [5]. TPB shows a significant difference around 689–687 eV, which correlate with the IR peaks around 885–850 cm<sup>-1</sup>. The C 1s spectra of LiFePO<sub>4</sub> cathodes also reflect the formation of organic surface species that contain C–O–C and –O–CO<sub>2</sub>– bonds (peaks around 286.5 and 290 eV). These results show that the amount of organic surface species on the LiFePO<sub>4</sub> cathode in the electrolyte with the various additives decrease in the following order: without additive > TPB > TMB. Thus, both XPS and IR measurements are consistent in demonstrating reactions between the LiFePO<sub>4</sub> surface and the electrolyte to form SEI films on the electrolyte surface, which occur with solution species (include impurities) at elevated temperature. Inorganic surface species such as LiF, Li<sub>x</sub>PF<sub>y</sub> and Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub>, as well as organic, carbonyl-containing surface species are formed. TMB can reduce inorganic surface species and carbonyl-containing surface species formation on the electrode surface. This in turn explains the low impedance of the LiFePO<sub>4</sub> cathode in electrolyte without TMP additive.

In summary, it is seen that TPB has low anion grabbing ability and participates in undesirable SEI formation. These effects are amplified by increasing TPB concentration and cycling temperature. TMB, on the other hand, has superior anion grabbing ability and has low participation in SEI formation. TMB also exhibits good temperature stability, resulting in batteries with good high temperature cyclability.

#### 4. Conclusion

The role of alkyl- and phenyl-substituted borate compounds in improving the electrochemical properties and high temperature performances of Li-ion battery electrolytes were explored. The data reported in this paper demonstrated that TMB is an effective electrolyte additive for improving the high temperature performance of LiFePO<sub>4</sub> cells. Of the TMB concentrations tested, the highest (0.1 M) showed the best performance. Test cells with 0.1 M TMB exhibited much higher capacity retention and suppressed thermal decomposition of the LiPF<sub>6</sub>-based electrolyte after 100 cycles at 60 °C. With the TMB additive, capacity fading was reduced to 47%. Addition of TMB to the electrolyte reduced the reaction of impurities with the electrolyte. The products of such reaction with the electrolyte negatively modified the SEI film formed on the electrode, which was confirmed by SEM, FTIR and XPS. The results clearly affirmed that 0.1 M TMB gave significantly improved performance. A lower concentration of TMB (0.05 M) also restrained electrolyte decomposition, but at significantly reduced levels. Another alkyl borate, TPB, was found significantly useless as an electrolyte additive with regard to fading at 60 °C, although it

was useful at 25 °C. TPB at 60 °C retained only 7% capacity after 100 cycles. The SEI layer formed by addition of TPB contained more surface film and hampered the interchange of lithium ions at the electrode surface. Our future work intends testing others boron-based compounds at different concentrations.

#### Acknowledgments

The authors are grateful for the financial support of this work by HOPAX Chemicals Mfg. Co., Taiwan, and the National Science Council of Taiwan under contracts number NSC 99-2221-E024-016 and NSC 100-3113-E-024-001-CC2.

#### References

- [1] O. Garcia-Moreno, M. Alvarez-Vega, F. Garcia-Alvarado, J. Garcia-Jaca, J.M. Gallardo-Amores, M.L. San-Juan, U. Amador, *Chem. Mater.* 13 (2001) 1570.
- [2] P. Zhang, X. Li, Z. Luo, X. Huang, J. Liu, Q. Xu, X. Ren, X. Liang, *J. Alloys Compd.* 467 (2009) 390.
- [3] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [4] N. Iltchev, Y. Chen, S. Okada, J.I. Yamaki, *J. Power Sources* 119–121 (2003) 749.
- [5] M. Koltypin, D. Aurbach, L. Nazar, B. Ellis, *Electrochem. Solid-State Lett.* 10 (2007) A40.
- [6] C.C. Chang, T.K. Chen, L.J. Her, G.T.K. Fey, *J. Electrochem. Soc.* 156 (11) (2009) A828.
- [7] C.C. Chang, T.K. Chen, *J. Power Sources* 193 (2009) 834.
- [8] S.S. Zhang, *J. Power Sources* 162 (2006) 1379.
- [9] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 1 (6) (1998) 239.
- [10] H.S. Lee, X. Sun, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 149 (11) (2002) A1460.
- [11] H.S. Lee, Z.F. Ma, X.Q. Yang, X. Sun, J. McBreen, *J. Electrochem. Soc.* 151 (2004) A1429.
- [12] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 146 (10) (1999) 3655.
- [13] H.S. Lee, X. Sun, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 145 (1998) 2813.
- [14] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 6 (2) (2003) A43.
- [15] C.L. Campion, W. Li, W.B. Euler, B.L. Lucht, B. Ravdel, J.F. DiCarlo, R. Gitzendanner, K.M. Abraham, *Electrochem. Solid-State Lett.* 7 (2004) A194.
- [16] A.M. Andersson, K. Edstrom, *J. Electrochem. Soc.* 148 (2001) A1100.
- [17] M. Herstedt, M. Stjern Dahl, T. Gustafsson, K. Edstrom, *Electrochem. Commun.* 5 (2003) 467.
- [18] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 4 (11) (2001) A184.
- [19] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 5 (11) (2002) A248.
- [20] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.* 149 (3) (2002) A355.
- [21] L.F. Li, H.S. Lee, H. Li, X.Q. Yang, K.W. Nam, W.S. Yoon, J. McBreen, X.J. Huang, *J. Power Sources* 184 (2008) 517.
- [22] Z.H. Chen, K. Amine, *Electrochem. Commun.* 9 (2007) 703.
- [23] K. Amine, J. Liu, I. Belharouak, *Electrochem. Commun.* 7 (2005) 669.
- [24] H.F. Jin, Z. Liu, Y.M. Teng, J.K. Gao, Y. Zhao, *J. Power Sources* 189 (2009) 445.
- [25] J. McBreen, H.S. Lee, X.Q. Yang, X. Sun, *J. Power Sources* 89 (2000) 163.
- [26] Z.C. Shi, A. Attia, W.L. Ye, Q. Wang, Y.X. Li, Y. Yang, *Electrochim. Acta* 50 (2008) 2665.
- [27] S. Okada, T. Yamamoto, Y. Okazaki, J.I. Yamaki, M. Tokunaga, T. Nishida, *J. Power Sources* 146 (2005) 570.
- [28] D. Aurbach, *J. Power Sources* 119–121 (2003) 497.
- [29] D. Aurbach, J.S. Gnanaraj, W. Geissler, M. Schmidt, *J. Electrochem. Soc.* 151 (2004) A23.
- [30] D. Aurbach, *J. Power Sources* 89 (2000) 206.
- [31] A.M. Andersson, D.P. Abraham, R. Haasch, S. MacLaren, J. Liu, K. Amine, *J. Electrochem. Soc.* 149 (2002) A1358.
- [32] S. Laruelle, S. Pilard, P. Guenot, S. Grugeon, J.-M. Tarascon, *J. Electrochem. Soc.* 151 (2004) A1202.